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(71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).

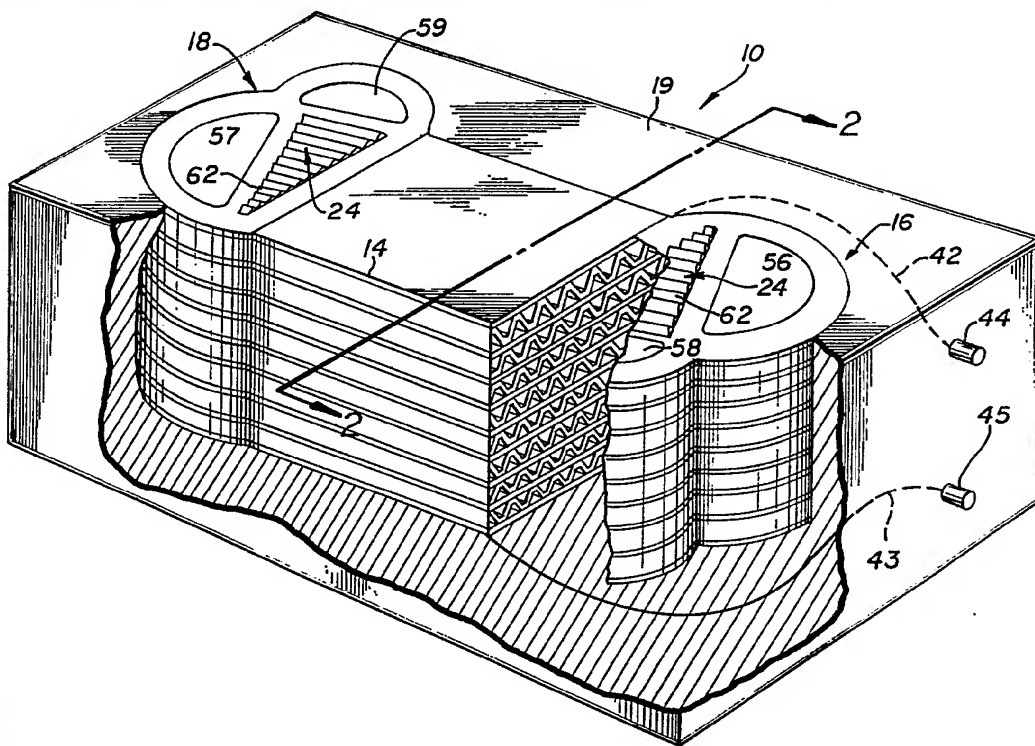
(72) Inventors: MINH, Nguyen, Q. ; 11701 Quartz Street, Fountain Valley, CA 90708 (US). HORNE, Craig, R. ; 2114B Marshall Field Lane, Redondo Beach, CA 90278 (US).

(74) Agent: MASSUNG, Howard, G.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).

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(54) Title: APPARATUS AND METHOD OF FABRICATING A MONOLITHIC SOLID OXIDE FUEL CELL

**(57) Abstract**

The invention details a two-step densifying process, method, and apparatus for making a solid oxide ceramic fuel cell (20). According to the invention, a limited number of anode (30)-electrolyte (31)-cathode (32) cells separated by a single or trilayer interconnect (33) are formed and densified. Subsequently, a plurality of the densified cells are stacked and further processed to form a monolithic array.

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APPARATUS AND METHOD OF FABRICATING A
MONOLITHIC SOLID OXIDE FUEL CELL

BACKGROUND OF THE INVENTION

This application is a continuation-in-part application of U.S. Serial Number 249,804 filed September 27, 1988, a divisional application of U.S. Patent Number 4,816,036.

The invention relates to solid oxide fuel cells and
5 more particularly to a method of fabricating the fuel cell core. A fuel cell is basically a galvanic conversion device that electrochemically reacts a fuel with an oxidant within catalytic confines to produce a DC electrical output. In a fuel cell, cathode material defines the
10 passageways for the oxidant and anode material defines the passageways for the fuel, and an electrolyte separates the cathode and anode materials. The fuel and oxidant fluids, typically as gases, are continuously passed through the cell passageways separated from one another. The fuel and
15 oxidant discharges from the fuel cell generally remove the reaction products and heat generated in the cell. The fuel and oxidant are the working fluids and as such are typically not considered an integral part of the fuel cell itself.

20 The type of fuel cell for which this invention has direct applicability is known as the solid electrolyte or solid oxide fuel cell, where the electrolyte is in solid form in the fuel cell. In the solid oxide fuel cell, hydrogen or a hydrocarbon fuel is preferably used as the
25 fuel and oxygen or air is used as the oxidant, and the operating temperature of the fuel cell is between 700° and 1,100° C.

The hydrogen passing through the fuel cell reacts with
oxide ions on the anode to yield water, which is carried
30 off in the fuel flow stream, with the release of electrons into the anode material. The oxygen reacts with the electrons on the cathode surface to form the oxide ions

which then pass into the electrolyte material. Electrons flow from the anode through an appropriate external load to the cathode, and the circuit is closed internally by the transport of oxide ions through the electrolyte. The
5 reaction process is well known and more thoroughly delineated in U.S. Patent Nos. 4,499,663 and 4,816,036.

The electrolyte isolates the fuel and oxidant gases from one another while providing a medium allowing oxygen ion transfer, as well as voltage buildup on opposite sides
10 of the electrolyte. Fuel and oxidant must diffuse away from the flow stream in the respective passageways to the electrolyte and react at or near the boundary of the electrodes (anode or cathode), and electrolyte, where electrochemical conversion occurs. The electrodes provide
15 paths for the internal movement of electrical current within the fuel cell to the cell terminals, which also connect with an external load. The operating voltage across each cell is on the order of 0.7 volts so the individual cells must be placed in electrical series to
20 obtain a useful load voltage.

U.S. Patent No. 4,476,198 (Ackerman, et al) discloses a monolithic core consisting only of materials active in the electrochemical reactions. The thin composite core walls are shaped to define small passageways. If the core
25 walls are constructed without deformation, they are predicted to have sufficient structural integrity to withstand the fluid pressures generated by gas flow through the passageways and the mechanical stresses due to the weight of the stacked core walls on one another. This
30 monolithic construction would beneficially increase the power density of the fuel cell because of its reduced size and weight.

U.S. Patent No. 4,476,196 (Poeppel, et al) discloses a monolithic core construction having the flow passageways
35 for the fuel and for the oxidant gases extended transverse to one another. The core construction provides that only anode material surround each fuel passageway and only cathode material surround each oxidant passageway, each

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anode and each cathode material further being selectively sandwiched at spaced opposing sides between electrolyte and interconnect materials. These composite anode and cathode wall structures are alternately stacked on one another

5 (with the separating electrolyte or interconnect material typically being a single common layer) whereby the fuel and oxidant passageways are disposed transverse or in a cross flow relationship to one another.

U.S. Patent No. 4,510,212 (Fraiola) discloses a core
10 construction having both parallel and cross flow paths for the fuel and the oxidant gases. Each interconnect wall of the cell is formed as a sheet of inert support material having therein spaced small plugs of interconnect material, the cathode and anode materials being formed as layers on
15 opposite sides of each sheet and being electrically connected together by the plugs of the interconnect material. Each interconnect wall is formed into a wavy shape and then connected along spaced, generally parallel, line-like contact areas between corresponding spaced pairs
20 of generally parallel electrolyte walls, operable to define one tier of generally parallel flow passageways for the fuel and oxidant gases. Alternate tiers are arranged to have the passageways disposed normal to one another.

Cellular type fuel cell cores (see U.S. Patent No.
25 4,476,198) of the prior art are made by the process whereby the compositions used for the four materials are put into four distinct slurries. Each slurry is then placed in a reservoir of a squeegee-type device which is pulled over a flat surface and hardens or plasticizes into a layer of the
30 material having the desired thickness. In this manner the electrolyte wall or interconnect wall is formed by a first layer of anode material followed by a layer of either electrode or interconnect material and finally by a layer of the cathode material. The layers are bonded together
35 since the binder system is the same in each layer.

Related U.S. Patent No. 4,816,036 (Kotchick) teaches another method of forming a cellular core, whereby the

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compositions for the four materials are individually mixed to a plastic consistency and subsequently hot rolled into thin sheets. The thin sheets can then be hot rolled into multilayer tapes, formed, stacked, and fired as a monolith
5 to produce the fuel cell with integral fuel and oxidant manifolding.

Theoretically, the fuel cell stack structure of the above-noted patents should provide exemplary power density. However, problems arise because the fuel cell stacks are
10 formed from arrays of anode and cathode sandwiching either an electrolyte or interconnect material in pliant or green form. The various green constituent layers are stacked on top of each other, appropriately oriented, to form the stack structure. The resultant stack structure is made up
15 of all green, or unsintered, constituent parts. As noted, the components of the stack are made of different materials, and thereby requiring one to try to match the coefficient of thermal expansion and firing shrinkage for the different materials as closely as possible to one
20 another to minimize separation problems. Fuel cell stacks which are made of green precursors which are all cosintered display poor performance due to microcracks which occur in the various layers as a result of the cosintering step if thermal expansion and firing shrinkage matched is not
25 achieved. A resulting cosintered stack produces significantly less current than its theoretical current density due to mixing of reactant gases which is the direct result of the micro-cracks in the stack. In addition, it is difficult to densify the interconnect under conditions
30 suitable for the other cell components. Inadequately densified interconnects allows cross-leakage of reactant gases.

A second problem arises when the multilayer fuel cell stacks of the prior art are densified in that there is
35 migration of the ceramic materials, primarily the interconnect material, into adjacent layers. This migration of the ceramic materials adversely effects the

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resulting component physical properties of density, porosity, and homogeneity. A third problem is the slumping of the corrugations during co-firing. As the size of the fuel cell structure increases the green corrugated layers are not stiff enough to support the structure weight during the heat treatment process. Accordingly, a processing method and the resulting fuel cell which eliminate the problems of microcracks, ceramic migration, and slumping would be desirable.

10

SUMMARY OF THE INVENTION

This invention relates to a solid oxide fuel cell and particularly to an improved method of making a core and integral manifolding for such a cell. An object of this invention is to provide an improved method for making a solid oxide fuel cell core of a complicated and compact cross section having many adjacent small passageways for containing the fuel and oxidant gases.

The method of fabricating the fuel cell core comprises the steps of first, individually mixing the anode, cathode, electrolyte and interconnect materials with a binder system. Second, forming thin tapes of the individual layers by either roll milling or slurry tape casting. Third, forming green state multilayer tapes preferably comprising an anode electrolyte-cathode or an anode-interconnect-cathode. Fourth, cutting and molding the respective green state multilayer tapes into the desired net shape elements. Fifth, assembling and bonding pairs of anode-interconnect-cathode elements (or alternatively simply interconnect elements) and anode-electrolyte-cathode elements. Sixth, densifying the assembled pairs of elements. Seventh, stacking and bonding the densified pairs of elements by wetting the contacting surfaces with a bonding agent to promote interbonding of the contacting surfaces to form a stacked assembly. Finally, densifying the stacked assembly to form a monolithic core assembly.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a perspective view, partially broken away for clarity of a fuel cell formed according to the present invention;

5 Fig. 2 is a partial, enlarged sectional view when taken along line 2-2 of Fig. 1;

Figs. 3 A & B are plan views of the individual electrolyte and interconnect elements;

10 Fig. 4 is a perspective view of an alternative configuration for a fuel cell formed according to the present invention;

Fig. 5 is a partial, enlarged sectional view of a portion of the fuel cell of Fig. 4.

15 Fig. 6 is a diagrammatic depiction of the two-step firing process required to form a fuel cell of the present invention.

Figs. 7 A, B, & C are exploded views of portions of alternative arrangements for the fuel cell core structure.

20 DETAILED DESCRIPTION OF THE INVENTION

Fig. 1 shows a monolithic solid oxide fuel cell (MSOFC) 10 of the present invention including a fuel cell core 14 and inlet and outlet manifolding, 16 and 18, at each end of the core 14. The core and manifolds are
25 located within and surrounded by suitable insulation 19. Not shown are supply lines connected to suitable fuel and oxidant sources.

Fig. 2 illustrates an enlarged cross-section of the fuel cell core 14 for the MSOFC 10 of Fig. 1. Within fuel
30 cell core 14 are formed a plurality of fuel passageways 20 and oxidant passageways 26 which are disposed parallel to one another and alternately adjacent one another. The fuel passageways 20 are preferably formed with only an anode material 30 defining the exposed fuel passageway walls 21
35 while the oxidant passageways 26 are preferably formed with only a cathode material 32 defining the exposed oxidant passageway walls 27. Adjacent fuel and oxidant passageways

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20 and 26 are separated by either an electrolyte wall 36 or by an interconnect wall 38. The electrolyte wall 36 comprises thin layers of electrolyte material 31 sandwiched between the anode material 30 and the cathode material 32 forming a trilayer. The interconnect wall 38 comprises a thin trilayer of interconnect material 33 sandwiched between anode material 30 and cathode material 32 to form a trilayer. Two interconnect walls 38 can define the limit of one cell unit 40, however in the overall fuel cell 10, two adjacent cell units 40 share an interconnect wall 38.

The anode, cathode, electrolyte, and interconnect materials 30, 32, 31, and 33 are selected and modified to comply with the following requirements: (1) electrically conductive aspects of the cathode, anode, and interconnect; (2) the ionic transport and electronic isolation aspect of the electrolyte; and (3) the gas porosity property of the cathode and anode and the gas impervious property of the electrolyte and interconnect. Likewise the structural integrity, thermal expansion and contraction ratios, and chemical compositions of the composite monolithic core are designed for the specific operational parameters of temperature, pressure, gas flow rates, voltage, and current densities necessary to provide optimal efficiency.

In a preferred embodiment of the invention, the interconnect and the electrolyte layers are thin (0.002-0.005 cm) while the sandwiching cathode and anode layers are perhaps the same thickness or possibly up to perhaps ten times this thickness (0.002-0.05 cm).

The MSOFC 10 provides increased power density due to the increased active exposure areas of fuel and oxidant per the corresponding unit flow path volume, and due further to having only the active materials (the anode, cathode, electrolyte, and interconnect) in the fuel cell core 14. The fuel and oxidant passageways 20 and 26, of the core 14 can be very small, and likewise the fuel and oxidant passageway walls 21, 27 can be thin but yet self supporting

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over the small distances across the defined fuel and oxidant passageways 20, 26, making possible shorter current paths and reduced resistance losses, and minimizing diffusion losses by eliminating thick supports entirely.

5 The inlet and outlet manifolds, 16 and 18, each include an oxidant conduit 58, 59 and a fuel conduit 56, 57 and a turning section generally designated by the numeral 24. Turning section 24 defines a plurality of fuel manifold passages 62 and a plurality of oxidant manifold
10 passages 64 as will be described later.

It is envisioned that the MSOFC 10 of the present invention can be used with parallel flow, counter flow or cross flow of the two working fluids. For the purpose of clarity it is assumed that a parallel flow system is being
15 used and therefore manifold 16 shall be referred to as the inlet manifold defining a fuel inlet conduit 56 and an oxidant inlet conduit 58 and manifold 18 shall be referred to as the outlet manifold defining a fuel outlet conduit 57 and an oxidant outlet conduit 59. Each manifold further
20 includes the turning sections 24.

Further to the above, it will be recognized by those skilled in the pertinent art that the electrochemically active fuel cell core of the MSOFC 10 is combined with conduits carrying fuel and oxidant to and from the fuel
25 cell core 14, making a complete functional fuel cell when attached to electrical conductors 42, 43, and encased in the thermal insulation 19. The conductors 42, 43 extend through the insulation 29 to terminals 44, 45 external thereto.

30 Unfortunately, the manifolding of a fuel cell is conventionally not electrochemically active so that the power and weight density of the fuel cell suffer, especially in the case of a parallel flow fuel cell. Also, conventionally, the conduits of the fuel cell are separate
35 pieces so that seals must be provided to prevent leakage of fuel and oxidant. As will be fully appreciated upon understanding this disclosure, these limitations of the

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conventional fuel cells are avoided by the preferred embodiments of the present invention.

Gaseous fuel is conveyed from a source (not shown) to the fuel inlet conduit 56 formed within the inlet manifold 16 for flow through the fuel manifold passages 62 and then through the fuel passageways 20 in the fuel cell core 14 toward the fuel outlet conduit 57 formed within the outlet manifold 18. Likewise, oxidant is carried from a source (not shown) to the oxidant inlet conduit 58 formed within the inlet manifold 16 for flow through the oxidant manifold passages 64 and in turn for flow through the oxidant passageways 26 toward the oxidant outlet conduit 59 formed within the outlet manifold 18. The fuel and oxidant react electrochemically across the electrolyte walls 36 separating the fuel and oxidant in the fuel cell core 14. Fuel and oxidant not consumed are discharged through the outlet manifold 18 and subsequently may be combusted with the other reaction products from the MSOFC 10 in an appropriate combustion chamber (not shown).

As can be best seen in Fig. 2, each electrolyte wall 36 is comprised of the layer of electrolyte material 31 sandwiched between the layer of anode material 30 and the cathode material 32. Electrolyte wall 36 electrochemically reacts the fuel and oxidant being conveyed in the fuel and oxidant passageways 20 and 26, respectively, to develop an electrical potential across the electrolyte wall 36.

Further, for all of the electrolyte walls 36 thus confined between any pair of adjacent interconnect walls (38a and 38b, for example), there is an in-series electrical hookup of the cell units (40a, 40b, for example). The electrolyte walls 36 are corrugated, or backfolded between the interconnect walls 38 so that the fuel and oxidant passageways 20 and 26 are likewise alternately disposed between any pair of adjacent interconnect walls 38.

Shown in Figs. 1 and 3 is the manifolding system to be used in association with the fuel cell core 14. The inlet manifold 16 and the outlet manifold 18 are similar to each

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other in their ducting of the fuel and oxidant flows. Each defines oxidant inlet and outlet conduits 58 and 59, and fuel inlet and outlet conduits 56 and 57, for connection to suitable oxidant and fuel sources. As will be described below the manifolding 16 and 18 and the fuel cell core 14 can be formed as an integral piece.

Shown in Figs. 3A and 3B are fuel cell core walls having inlet and outlet manifolds 16 and 18 integral therewith. Fig. 3A discloses the electrolyte wall 36 and Fig. 3B discloses the interconnect wall 38. Shown in Fig. 3A are electrolyte wall impressions or corrugations 68 extending between the manifolds 16 and 18, and which, when alternatively stacked with the interconnect walls 38, form the fuel and oxidant passageways 20, 26. At each end of the corrugations 68 of the electrolyte wall 36 are a plurality of manifold corrugations 70 which extend parallel with each other and with the manifold corrugations 70 at the opposite end of the fuel and oxidant passageways 20, 26. Each manifold corrugation 70 has a height less than the height of the fuel and oxidant passageways 20 and 26 (see Fig. 5). Inlet and outlet fuel manifold passageways 62 extend from the ends of the fuel cell core fuel passageways 20 to the fuel inlet and outlet manifolds 16 and 18. Likewise, inlet and outlet oxidant manifold passageways 64 extend from the ends of the oxidant passageways 26 to the oxidant inlet and outlet conduits 58 and 59 formed internally to manifolds 16 and 18.

An alternative construction of a cross flow monolithic solid oxide fuel cell (MSOFC) 110 is depicted in Fig. 4 and exploded Figs. 5 and 7, and including a core section 114, oxidant inlet manifold 116, fuel inlet manifold 117, oxidant outlet manifold 118 and fuel outlet manifold 119. An exploded portion of the cross flow MSOFC 110 is depicted in Fig. 5. In the cross flow MSOFC 110, an anode 130, electrolyte 136, and a cathode 132 are formed into an electrolyte trilayer 142. Another anode 130' and cathode 132' are formed into a corrugated, backfolded or ribbed

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(Fig. 7) configuration and attached to opposite sides of the electrolyte 131 or the electrolyte trilayer 142, adjacent the respective similar anode 130 and corrugated cathode 132. The corrugated anode 130' and cathode 132' layers are arranged with the corrugations at crossing angles to one another, preferably at right angles. Interconnect layers 138 are stacked and attached to the corrugated anode 130' and cathode 132' at opposite sides of the respective corrugations from the planar electrolyte trilayer 142. A plurality of these stacked elements form a complete cross flow MSOFC 110. The method of forming this cross flow MSOFC 110 is analogous to the method of forming the parallel flow configuration of Figs. 1-3, as more fully discussed below.

15

PREFERRED METHOD OF FABRICATING THE FUEL CELL

Shown in Fig. 6 is a schematic diagram of the process to manufacture a MSOFC 10 of the present invention. Ceramic powders for each of the materials: strontium-doped lanthanum manganite for the cathode, yttria-stabilized zirconia for the electrolyte lanthanum chromite-doped with magnesium, calcium cobalt, or strontium for the interconnect and a cermet of cobalt or nickel metal with stabilized zirconia for the anode, are first prepared so that the particle size ranges from approximately 1 micron to 10 microns. The respective powders are then mixed with a desired binder and plasticizer in a high intensity mixer 80. For example, to form the electrolyte material, zirconia and yttria are mixed in approximate percentages of 87 to 13 by weight. The binder and plasticizer make up approximately 10 - 40%, by weight, of the total mix and preferably approximately 18%. The amounts of binder and plasticizer being approximately equal. Porosity may be controlled by using larger sized particles, by the addition of pore formers, or by the use of the higher percentage of binder.

Typically, the binder used can be selected from the

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group comprising: synthetic rubber, thermosetting plastics, polyvinyl alcohol or polymer systems which thermally decompose without cross-linking. The plasticizer chosen is one that is pliable, elastic, and allows low temperature forming of the binder system, e.g. butyl benzyl phthalate, or solvents of the thalate group.

The ceramic powder, binder and plasticizer are combined in the high intensity mixer 80 at room temperature. The mixing disperses the ceramic powder particles and coats each ceramic particle with binder. The mixing action also raises the temperature through friction to 150°C and softens the plasticizer. Typically, the time for mixing can be 0.5 to 10 minutes with 2 minutes generally being sufficient.

The mixed material is then removed from the mixer and formed into tapes, preferably immediately after mixing to retain the heat generated by the mixing. As shown, the tape forming step is carried preferably out by a roll mill 82. Alternatively, however, the tapes could be formed by other methods including extruding, pressing or tape casting. In the roll milling process, each roller is generally heated to approximately 10° - 150°C, depending on the material and the desired thickness, to assist in the rolling operation. Each material i.e. the anode, cathode, electrolyte and interconnect materials, is individually roll milled into tapes 30, 32, 31 and 33 of the desired thickness. It should be noted that the numerals 30, 31, 32, and 33 will hereinafter designate the material as well as a tape or element formed of that material. Thereafter, a multilayer electrolyte or interconnect wall tape 36 or 38 is roll-milled from at least three of the other tapes, i.e. 30, 31 or 33, and 32. During this step each tape is friction bonded to the adjacent tape(s). It is important that no voids are formed between or within the respective tape layers during this rolling step. The resulting multilayer electrolyte or interconnect wall tapes 36, 38 may be further calendared if required to reduce the

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thickness.

To provide passageways for the fuel and oxidant through the MSOFC 10. The plurality of fuel and oxidant passageways 20, 26 are formed, for example extending along the anode 30 and cathode 32 respectively. In order to increase the efficiency of the parallel or counterflow MSOFC 10, 110, it is advantageous to form the passageways 20, 26 by corrugating the trilayer electrolyte tape 36 to achieve greater surface area. This can be accomplished by compression molding, vacuum forming or by gear forming. During this operation, it is important not to get any material flow, thereby retaining the desired layer thicknesses.

Alternatively, for the cross flow MSOFC 110 configuration of Fig. 4, a single trilayer electrolyte tape 142 is first formed preferably by the roll milling process or alternatively by a tape casting, extruding or pressing process. As shown for example in Figs. 7 A, B, & C, ribs 150, 152; fins 154, 156; or posts 160, 162; may be formed in the exposed surface of the anode 130 and cathode 132 respectively by displacing contiguous portions of the respective surfaces of the anode 130 and cathode 132 from the plane of the pre-existing flat surface. This may be accomplished by compression molding or pressing, rolling, or by cutting groves into the trilayer electrolyte 142. As may be readily appreciated, the fins 154, 156 or posts 160, 162 may be so arranged as to force the respective fuel and oxidant to traverse a tortuous pathway along the surfaces of the trilayer electrolyte 142.

Alternatively, single layer sheets of anode 130' and cathode 132' may be first roll milled or tape cast, then formed by a compression molding or similar technique into a corrugated or backfolded configuration, for attachment to the trilayer electrolyte tape 142 as discussed below.

In addition, a planar single layer of interconnect 138, or an (anode-interconnect-cathode) interconnect trilayer 140, is formed by either the roll milling or tape

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casting processes described above. The resulting trilayer tapes 36, 38, 140, 142 and single layer tapes 130', 132', 138 for the respective parallel or crossflow assemblies are then cut or pressed into a plurality of individual elements 5 having preferred gross net shapes (numbered similarly to their respective tapes from which the elements are formed). These gross net shapes preferably include the walls for the manifolds 16, 18, 116, 117, 118, and 119, as well as the corrugations for the passageways 20, 26, 62, 64, if 10 required.

Next, a limited number of the trilayer electrolyte and interconnect elements 36, 38 for the parallel flow configuration, or a single trilayer electrolyte element 142 and one each of the anode elements 130', and cathode 15 elements 132' are stacked and bonded to one another. This is preferably accomplished by wetting the contacting surfaces of the elements with a solution which will partially dissolve the entrained binder and/or plasticizer within the elements. By way of example, an isopropyl 20 alcohol solution can be brushed or sprayed onto the elements to dissolve the binder. After the contacting elements are assembled, the alcohol solution evaporates and the binder joins the contacting surfaces. For the parallel flow configuration, the corrugated trilayer 36 electrolyte 25 is bonded to the interconnect trilayer 38 (or interconnect layer 38'). For both the parallel flow and cross flow configurations, this process of joining the green state trilayer elements is preferably limited to less than ten complete cells, and optimally may be limited to single 30 pairs of electrolyte trilayer elements 36 and interconnect trilayer elements 38 (or interconnect elements 38').

The assembled elements are then heat treated, preferably in a furnace or microwave oven 134, by any one or a combination of radiant, convective, or microwave 35 heating to a temperature sufficient to sinter the respective anode, electrolyte, cathode and interconnect ceramics. During this heating process, the respective

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ceramic materials are preferably sintered to between twenty five percent to one hundred percent of their desired final density, as measured by the percentage of shrinkage during sintering. Alternatively, the heating process proceeds to
5 a temperature sufficient to sinter the respective ceramic materials to a percentage of the desired final density for the respective materials such that subsequent heating and sintering will result in compatible shrinkage of all ceramic materials. The sintering temperature is selected
10 to achieve the desired properties, including a dense electrolyte, porous anode and cathode, and dense interconnect. The interconnect elements 38, 38', 138, or 140 may be heat treated individually, to a temperature sufficient to sinter the interconnect ceramic material to a
15 percentage of the desired final density for the interconnect ceramic material such that the interconnect ceramic material will not diffuse into adjacent layers of the stacked array during subsequent heating and sintering of the stacked array. The corrugated electrolyte trilayer
20 36, or the assembled electrolyte trilayer 142 and anode 130' and cathode 132' are separately heat treated as above. These densified components are then preferably allowed to cool to a temperature which allows handling. This initial heat treatment may proceed to the point of only partially
25 sintering the assemblies. Thus, the assembled elements are sintered to at least about twenty five percent of the total sintering required for the final fuel cell as measured by the shrinkage of the materials required to achieve the final desired densities. Preferably, the assembled
30 elements are sintered to between eighty to one hundred percent of their final densities.

The sintered and densified components are then assembled and bonded in their proper sequences into a monolithic structure or stacked assembly 48. During the
35 assembly of the densified components, the contacting surfaces are wetted with a bonding agent 50. The bonding agent 50 is preferably a viscous slurry of anode material

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or cathode material, and possibly interconnect material, mixed with a compatible binder, plasticizer, and solvent which is brushed 54 or sprayed onto the elements. The selection of the component materials incorporated into the bonding agent 50 is dependent upon the surfaces to be interbonded. To bond two cathode surfaces only cathode materials are used, and similarly to bond an anode surface to an interconnect surface both anode and interconnect materials are used. Similarly, to bond two anode surfaces, only anode materials are used. However, to bond a cathode surface to an interconnect surface both cathode and interconnect materials may be used. By way of example, the bonding agent 50 is formed by combining the selected ceramic component materials with polyvinyl butyryl resin, butyl benzyl phthalate, and isopropyl alcohol into a viscous slurry. Alternatively, the bonding agent 50 may be formed by combining the selected ceramic component materials with materials such as a ceramic paste base, zirconia cement, cellulose-ether compound, a glass-ceramic, or an organo-metallic sol-gel material. Platinum ink or platinum powder may also be added to the bonding agent 50 to improve the electrical conductivity within the MSOFC 20 (or 110).

The stacked assembly 48 is then heat treated, preferably in a furnace or microwave oven 134 operating at temperatures of 1000-1400°C, to sinter and densify the bonding agent 50. By way of example, the stacked assembly 48 is heated at ramp rates of 10-50°C per hour to 1200°C. The temperature is maintained at 1200°C for 1 hour, and then the stacked assembly 48 is allowed to gradually cool down. Microwave heating is preferably carried out at a frequency of 28 Giga-Hertz. In this heat treating procedure, the organics and volatile components of the bonding agent 50 are burned out or outgassed and the component materials (anode, cathode, and interconnect) are sintered to bond adjacent contacting surfaces of the previously sintered and densified subassemblies. This two step sintering and

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densifying process reduces the thermal induced cracking, slumping of the corrugations, and diffusion of the component materials into adjacent layers, while allowing assembly of a monolithic core having a very high number of
5 individual cells. It should be noted that during the assembly of the sintered subassemblies into the stacked monolith and during the heat treating of the monolith, a compressive force may be applied to promote contact and interbonding at the adjacent surfaces.

10 It should be evident from the foregoing description that the present invention provides many advantages in the field of manufacturing monolithic solid oxide fuel cells. Although preferred embodiments are specifically illustrated and described herein, it will be appreciated that many
15 modifications and variations of the present invention are possible in light of the above teaching to those skilled in the art. It is preferred, therefore, that the present invention be limited not by the specific disclosure herein, but only by the appended claims.

20

CLAIMS:

1. A method of constructing a monolithic solid oxide fuel cell (10) comprising the steps of:
 - mixing ceramic powders required to make an anode (30), a cathode (32), an electrolyte (31), and an interconnect (33) each individually with a binder system to form a batch of each of said materials;
 - forming thin tapes of each of said material batches;
 - attaching said anode (30) tape to said electrolyte (31) tape and said cathode (32) tape on an opposite side of said electrolyte (31) tape to form a trilayer electrolyte (36) tape;
 - shaping said trilayer electrolyte (36) tape to form fuel flow pathways (20) extending along said anode (30), and oxidant flow pathways (26) extending along said cathode (32) of said trilayer electrolyte (36) tape;
 - cutting said trilayer electrolyte (36) tape to form a plurality of trilayer electrolyte (36) elements having a desired gross net shape;
 - cutting said interconnect (33) tape to form a plurality of interconnect elements (38) having a desired gross net shape;
 - heating said trilayer electrolyte (36) elements and said interconnect elements (38) to a temperature sufficient to cause removal of the binder system and at least initiated sintering of the respective ceramic materials;
 - stacking a plurality of said at least partially sintered trilayer electrolyte (36) elements alternately with a plurality of said interconnect elements (38), subsequent to said heating step, to form a stacked array (48); and
 - processing said stacked array (48) to bond the contacting surfaces of said alternately stacked trilayer electrolyte (36) and interconnect elements (38).
2. The method of claim 1, wherein said heating step is further characterized by:

raising the temperature of said respective trilayer electrolyte (36) elements and said interconnect elements (38) by any one or a combination of heating processes selected from the group consisting of radiant, convective, and microwave heating to a temperature sufficient to sinter the respective ceramic materials to at least 25% of the total material shrinkage resulting from sintering the ceramic materials to a desired final density.

3. The method of claim 1, wherein said heating step is further characterized by:

raising the temperature of said trilayer electrolyte (36) elements and said interconnect elements (38) to a temperature sufficient to sinter the respective ceramic materials to a percentage of the desired final density for said respective materials such that subsequent heating and sintering of said stacked array (48) will result in compatible shrinkage of all ceramic materials in said stacked array (48) and said interconnect (33) ceramic material will not diffuse into adjacent layers of said stacked array (48) during subsequent heating and sintering of said stacked array (48).

4. A method of constructing a monolithic solid oxide fuel cell (10) having a plurality of stacked cells (40), each cell (40) including a cathode (32), an electrolyte (31), and an anode (30), said cells (40) being separated from one another by an interconnect (33), comprising the steps of:

assembling a plurality of trilayer electrolyte (36) elements each including respective layers of at least partially sintered cathode (32) ceramic materials, electrolyte (31) ceramic materials, and anode (30) ceramic materials, said trilayer electrolyte (36) elements shaped to define fuel and oxidant flow pathways (20, 26) formed into the said trilayer electrolyte (36) elements having a desired configuration;

forming a plurality of interconnect elements (38) each including at least partially sintered interconnect (33) ceramic materials in a desired configuration;

wetting one surface of said interconnect elements (38) and the surface of said anode (30) of said trilayer electrolyte (36) elements with an anode bonding agent, said anode bonding agent including powders of said anode (30) ceramic material, a binder system materials, and a solvent mixed into a viscous slurry;

wetting the opposite surface of said interconnect elements (38) and the surface of said cathode (32) of said trilayer electrolyte (36) elements with a cathode bonding agent, said cathode bonding agent including powders of said cathode (32) ceramic material, said binder system materials, and a solvent mixed into a viscous slurry;

stacking a plurality of said at least partially sintered trilayer electrolyte (36) elements alternately with a plurality of said interconnect elements (38) to form a stacked array (48); and

processing said stacked array (48) to bond the contacting surfaces of said alternately stacked trilayer electrolyte (36) and interconnect elements (38).

6. The method according to any of claims 1-5,, further characterized by:

selecting a cermet of cobalt or nickel metal with stabilized zirconia for said anode (30), strontium-doped lanthanum manganite for said cathode (32), yttria-stabilized zirconia for said electrolyte (31), and doped lanthanum chromite for said interconnect (33);

selecting said binder system materials of said anode bonding agent and said cathode bonding agent for compatibility with said anode (30), cathode (32), electrolyte (31), and interconnect (33) materials, said binder system materials including a binder selected from the group consisting of synthetic rubber, plastics, polyvinyl alcohol, polyvinyl butyryl resin, and polymer

systems which thermally decompose without cross linking,
and a plasticizer selected from the group consisting of
butyl benzyl phthalate and solvents of the phthalate group;
and

- 5 selecting isopropyl alcohol for said solvent of said
anode bonding agent and said cathode bonding agent.

7. The method according to any of claims 1-5,
wherein said stacking step is further characterized by:
- 10 wetting adjacent surfaces of said interconnect
elements (38) and said anode (30) of said trilayer
electrolyte (36) elements with an anode bonding agent;
 wetting adjacent surfaces of said interconnect
elements (38) and said cathode (32) of said trilayer
15 electrolyte (36) elements with a cathode bonding agent,
said bonding agents including powders of said anode (30)
ceramic material for said anode bonding agent, and said
cathode (32) ceramic material for said cathode bonding
agent respectively, mixed with a bonding material.

20

8. The method according to of claim 7 wherein said
bonding material further comprises:
- a binder selected from the group consisting of
synthetic rubber, plastics, polyvinyl alcohol, polyvinyl
25 butyryl resin, cellulose, and polymer systems which
thermally decompose without cross linking;
 a plasticizer selected from the group consisting of
butyl benzyl phthalate and solvents of the phthalate group;
and
- 30 a solvent, said ceramic materials, said binder, said
plasticizer, and said solvent mixed together to form a
viscous slurry.

9. The method of claim 7 wherein said bonding
35 material further comprises:
- a ceramic paste material including at least one of the
materials selected from the group consisting of ceramic

cements, glass ceramics, an organo-metallic sol gel material, and zirconium oxide.

10. The method of any of the above claims 1-5,
5 wherein said processing step is further characterized by:
 raising the temperature of said stacked array (48) by
any one or a combination of heating processes selected from
the group consisting of radiant, convective, and microwave
heating to a temperature sufficient to sinter the
10 respective ceramic materials to their desired final
density.

11. The method according to any of claims 1-5,
wherein said step of shaping said trilayer electrolyte (36)
15 tape to form said fuel and oxidant flow pathways is further
characterized by:
 deforming the respective surfaces of said anode (30)
layer and said cathode (32) layer of said trilayer
electrolyte (36) tape by displacing contiguous portions of
20 said surfaces from the plane of the pre-existing flat
surface, leaving raised surface portions to form a ribbed,
finned, or pillared anode (30) and cathode (32) surface
configuration.

25 12. The method of any of claims 1-5, wherein said
step of shaping said pathways is further characterized by:
 deforming said trilayer electrolyte (36) elements to a
corrugated or backfolded configuration.

30 13. The method according to any of claims 1-5,
further characterized by:
 configuring said plurality of trilayer electrolyte
(36) elements and said plurality of interconnect elements
(38) to include aligned integral fuel inlet, fuel outlet,
35 oxidant inlet, and oxidant outlet manifolds (56, 57, 58, 59
respectively) at spaced apart locations;
 enclosing said fuel pathway (20) extending along said

anode (30) of said plurality of electrolyte (31) layers such that said fuel pathways (20) extend from said fuel inlet manifold (56) to said fuel outlet manifold (57); and enclosing said oxidant pathways (26) extending along
5 said cathode (32) of said plurality of electrolyte (31) layers such that said oxidant pathways (26) extend from said oxidant inlet manifold (58) to said oxidant outlet manifold (59).

10 14. An apparatus for constructing a monolithic solid oxide fuel cell (10) having a plurality of stacked cells (40), each cell (40) including a cathode (32), an electrolyte (31), and an anode (30), said cells (40) being separated from one another by an interconnect (33), the
15 apparatus comprising:

a plurality of electrolyte (31) elements each including respective layers of at least partially sintered cathode (32) ceramic materials, electrolyte (31) ceramic materials, and anode (30) ceramic materials, said
20 electrolyte (31) elements configured to include fuel and oxidant flow pathways, said electrolyte (31) elements shaped in a desired configuration;

a plurality of interconnect elements (38) each including at least partially sintered interconnect (33)
25 ceramic materials in a desired configuration, said interconnect elements (38) alternately stacked with said plurality of electrolyte (31) elements to form a stacked array (48); and

bonding agent means for bonding said at least
30 partially sintered interconnect elements (38) to said at least partially sintered electrolyte (31) elements.

15. The apparatus of claim 14 wherein said bonding agent means further comprises:

35 an anode bonding agent including powders of said anode (30) ceramic material, a binder system material, and a solvent mixed into a viscous slurry for bonding one surface

of said interconnect elements (38) to said anode (30) of said electrolyte (31) elements; and

a cathode bonding agent including powders of said cathode (32) ceramic material, said binder system material, and a
5 solvent mixed into a viscous slurry for bonding the
opposite surface of said interconnect elements (38) to said cathode (32) of said electrolyte (31) elements.

16. The apparatus of claim 15, wherein said anode
10 bonding agent and said cathode bonding agent each further include interconnect (33) ceramic materials or platinum powder mixed into said respective viscous slurries.

17. The apparatus of claim 15 wherein said bonding
15 agent means further comprises:

a ceramic paste material including at least one of the materials selected from the group consisting of ceramic cements, glass ceramics, an organo-metallic sol gel material, and zirconium oxide.

20

18. A bonding agent for use in bonding the contacting surfaces of pre-sintered ceramic elements of a monolithic solid oxide fuel cell (10), said bonding agent comprising:

ceramic materials selected from the group consisting
25 of anode (30) ceramics, cathode (32) ceramics, and interconnect (33) ceramics;

a binder selected from the group consisting of synthetic rubber, plastics, polyvinyl alcohol, polyvinyl butyryl resin, and polymer systems which thermally
30 decompose without cross linking;

a plasticizer selected from the group consisting of butyl benzyl phthalate and solvents of the phthalate group; and

a solvent, said ceramic material, said binder, said
35 plasticizer, and said solvent mixed together to form a viscous slurry.

19. A monolithic solid oxide fuel cell (10) constructed according to the process steps of:

mixing ceramic powders required to make an anode (30), a cathode (32), an electrolyte (31), and an interconnect (33) each individually with a binder system to form a batch of each of said materials;

forming thin tapes of each of said material batches; attaching said anode (30) tape to said electrolyte (31) tape and said cathode (32) tape on an opposite side of said electrolyte (31) tape to form a trilayer electrolyte (36) tape;

shaping said trilayer electrolyte (36) tape to form fuel flow pathways extending along said anode (30), and oxidant flow pathways extending along said cathode (32) of said trilayer electrolyte (36) tape;

cutting said trilayer electrolyte (36) tape to form a plurality of trilayer electrolyte (36) elements having a desired gross net shape;

cutting said interconnect (33) tape to form a plurality of interconnect elements (38) having a desired gross net shape;

heating said trilayer electrolyte (36) elements and said interconnect elements (38) to a temperature sufficient to cause removal of the binder system and at least initiated sintering of the respective ceramic materials;

stacking a plurality of said at least partially sintered trilayer electrolyte (36) elements alternately with a plurality of said interconnect elements (38), subsequent to said heating step, to form a stacked array (48); and

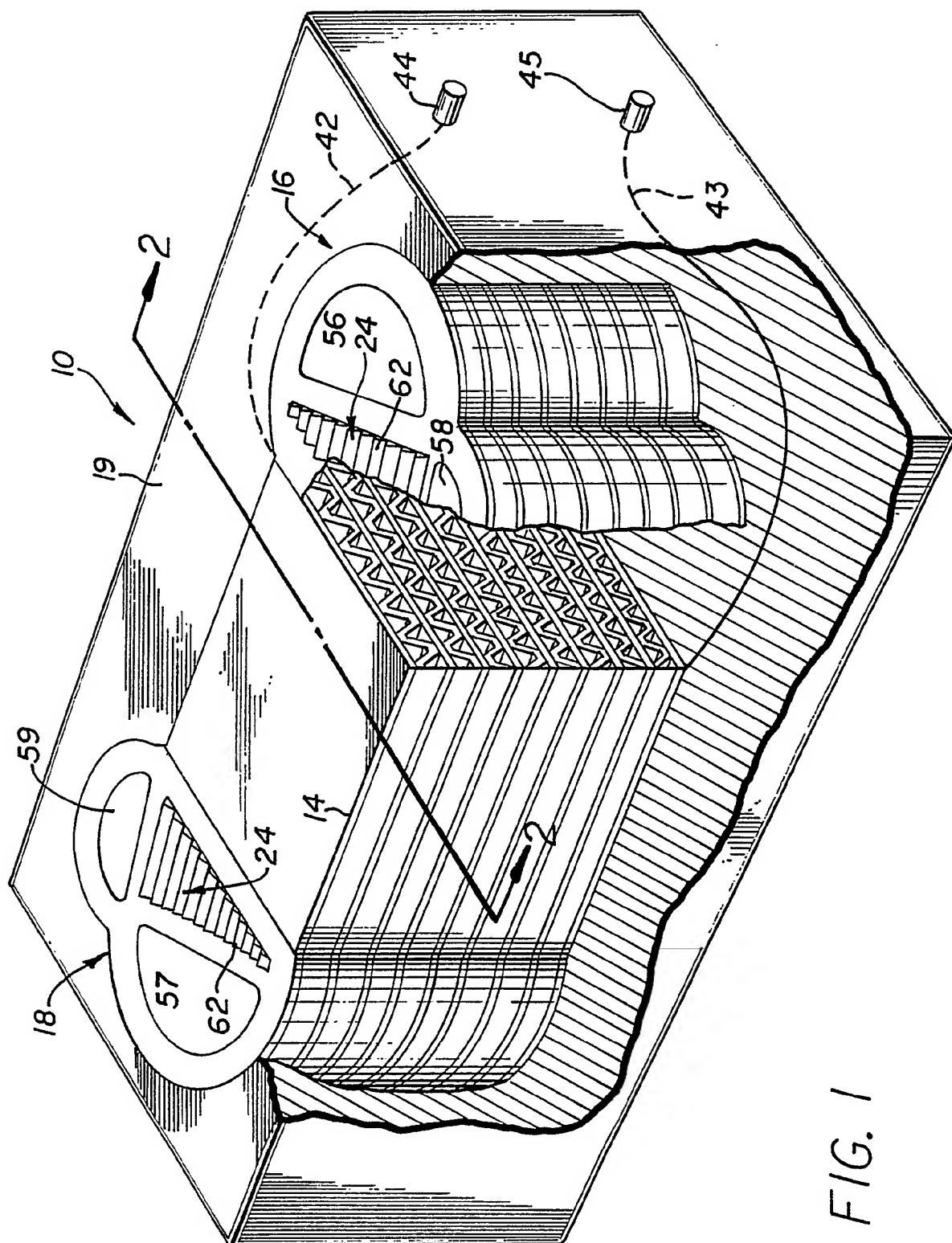
processing said stacked array (48) to bond the contacting surfaces of said alternately stacked trilayer electrolyte (36) and interconnect elements (38).

20. A monolithic solid oxide fuel cell (10) having a plurality of stacked cells (40), each including a cathode (32), an electrolyte (31), and an anode (30), said cells

(40) being separated from one another by an interconnect (33), constructed according to the process steps of:

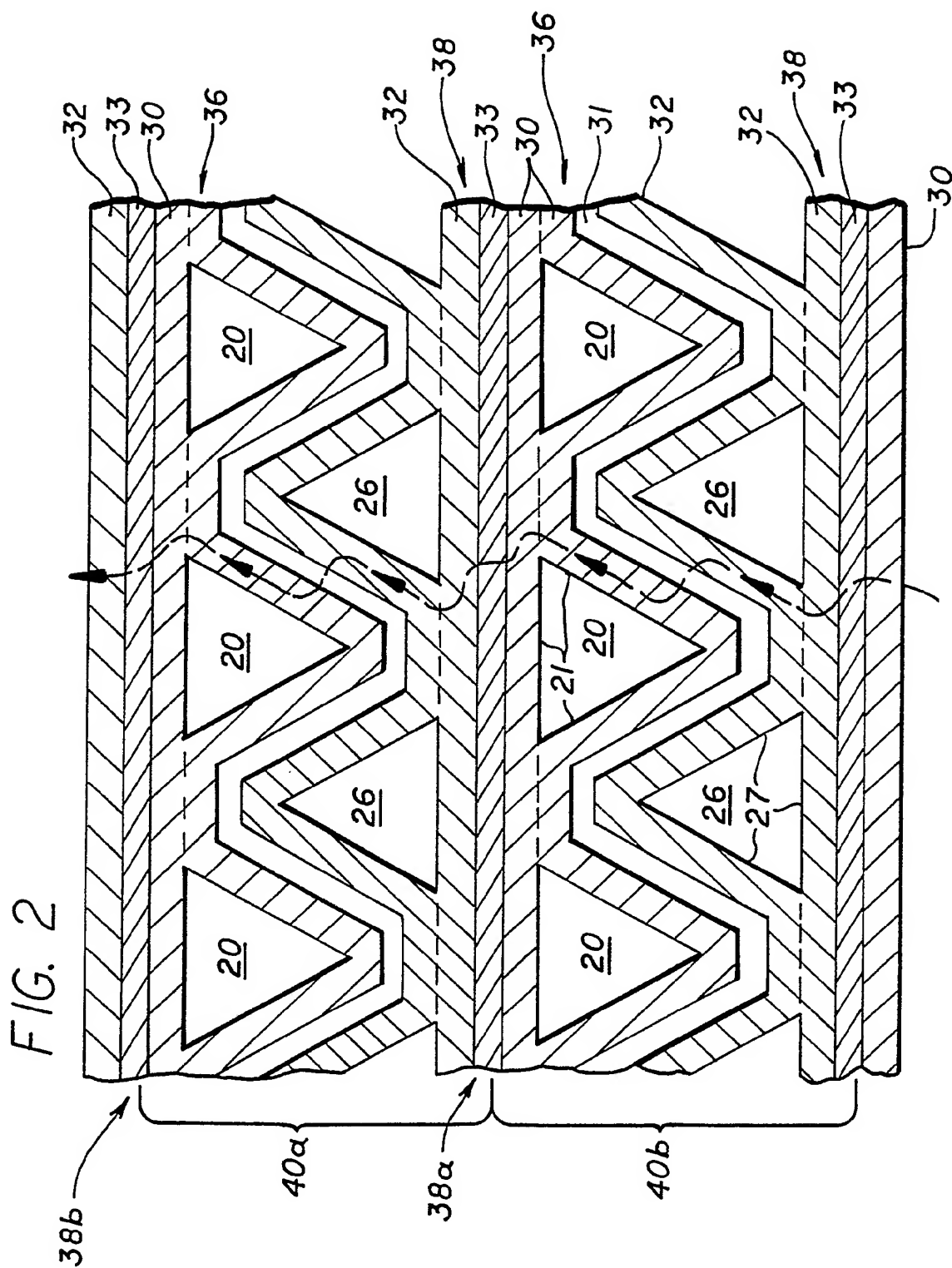
- assembling a plurality of trilayer electrolyte (36) elements each including respective layers of at least
5 partially sintered cathode (32) ceramic materials, electrolyte (31) ceramic materials, and anode (30) ceramic materials, said trilayer electrolyte (36) elements including fuel and oxidant flow pathways (20, 26) formed into the respective surfaces of said anode (30) layer and
10 said cathode (32) layer by displacing contiguous portions of said surfaces from the plane of the pre-existing flat surface leaving raised surface portions, said trilayer electrolyte (36) elements having a desired configuration;
- forming a plurality of interconnect elements (38) each
15 including at least partially sintered interconnect (33) ceramic materials in a desired configuration;
- wetting one surface of said interconnect elements (38) and the surface of said anode (30) of said trilayer electrolyte (36) elements with an anode bonding agent, said
20 anode bonding agent including powders of said anode (30) ceramic material, said interconnect (33) ceramic materials, a binder system materials, and a solvent mixed into a viscous slurry;
- wetting the opposite surface of said interconnect
25 elements (38) and the surface of said cathode (32) of said trilayer electrolyte (36) elements with a cathode bonding agent, said cathode bonding agent including powders of said cathode (32) ceramic material, said interconnect (33) ceramic material, said binder system materials, and a
30 solvent mixed into a viscous slurry;
- stacking a plurality of said at least partially sintered trilayer electrolyte (36) elements alternately with a plurality of said interconnect elements (38) to form a stacked array (48); and
- 35 processing said stacked array (48) to bond the contacting surfaces of said alternately stacked trilayer electrolyte (36) elements and interconnect elements (38).

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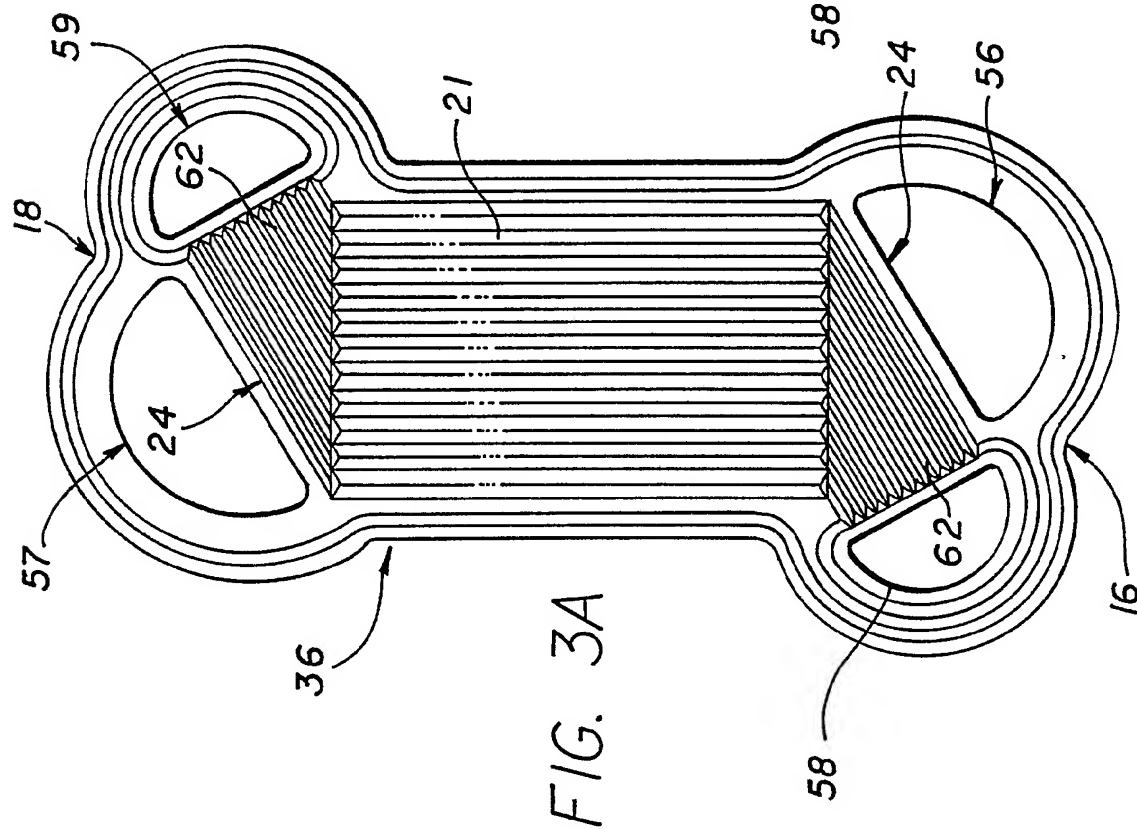
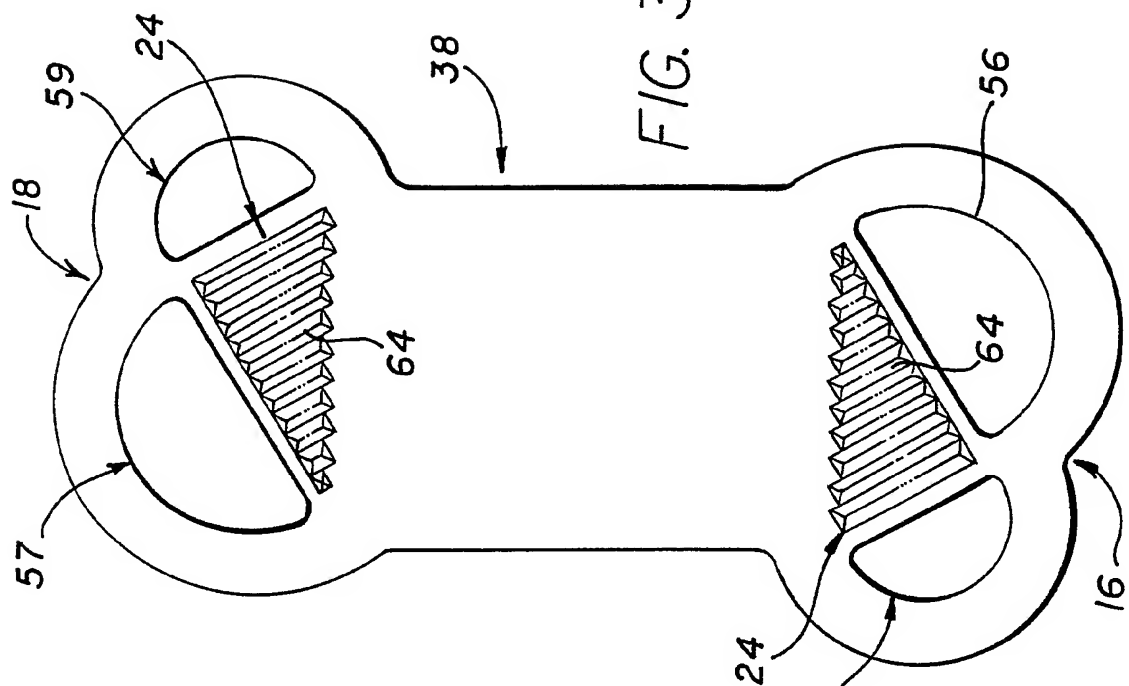
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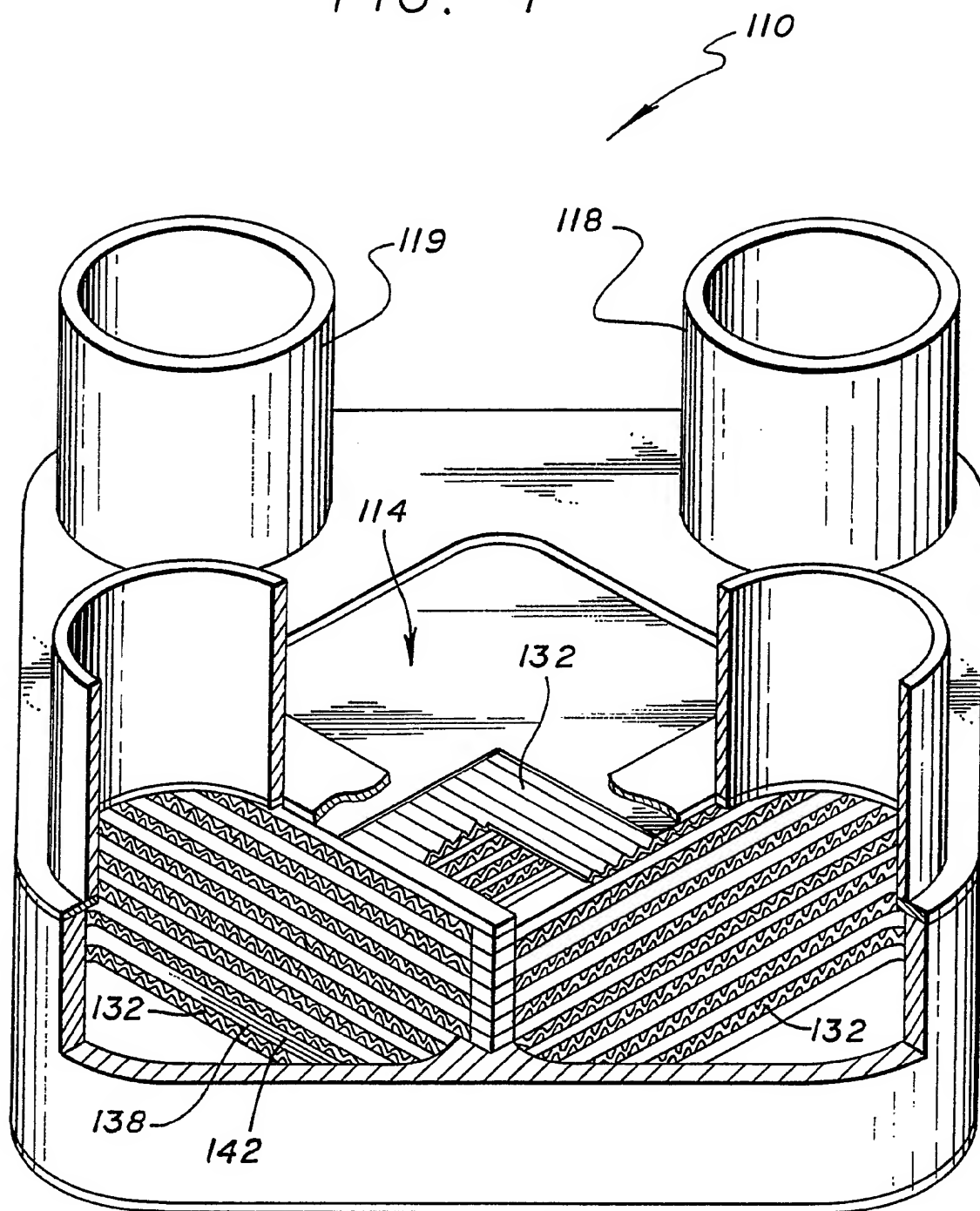
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FIG. 4

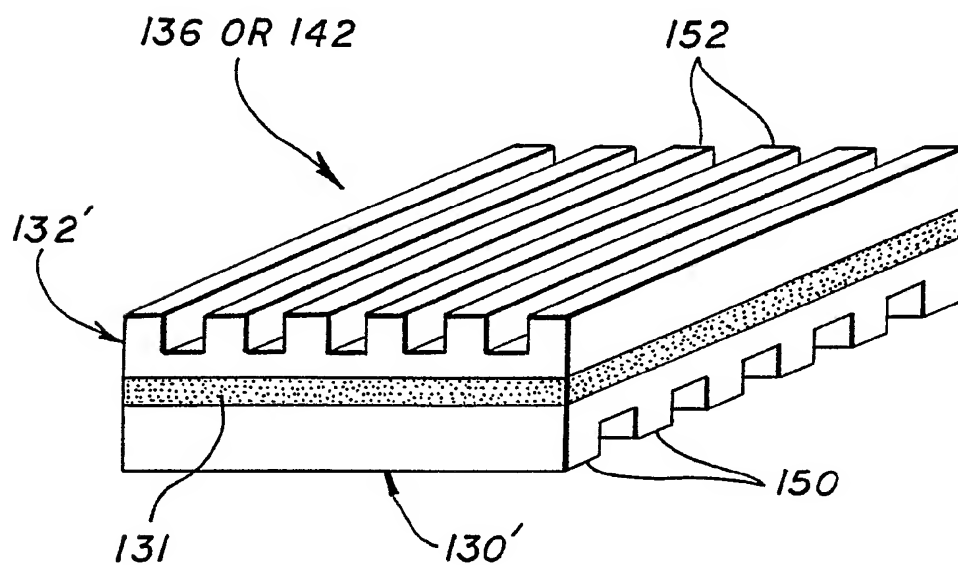
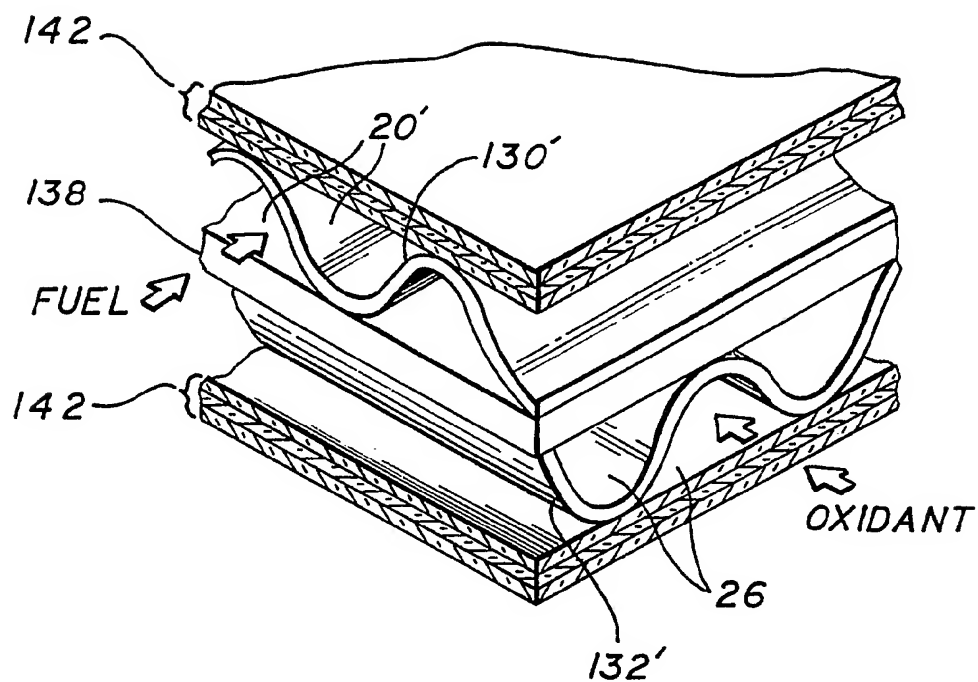
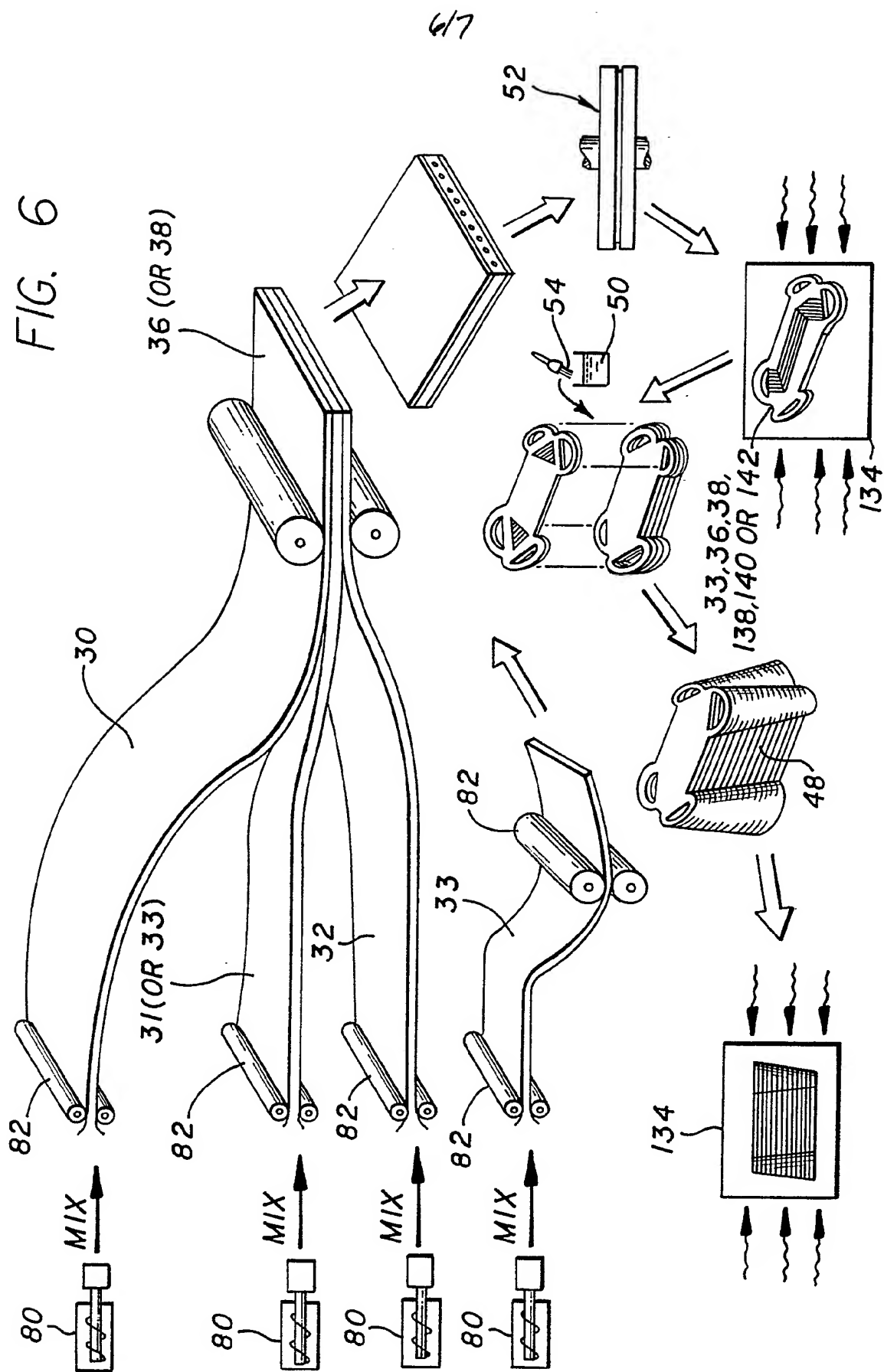
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FIG. 5

FIG. 7A

FIG. 6



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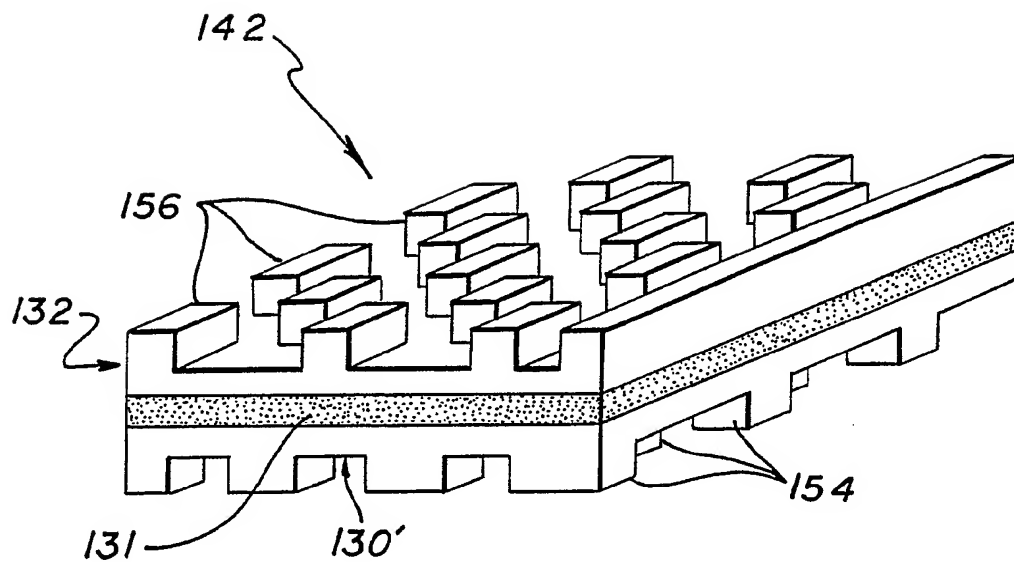


FIG. 7B

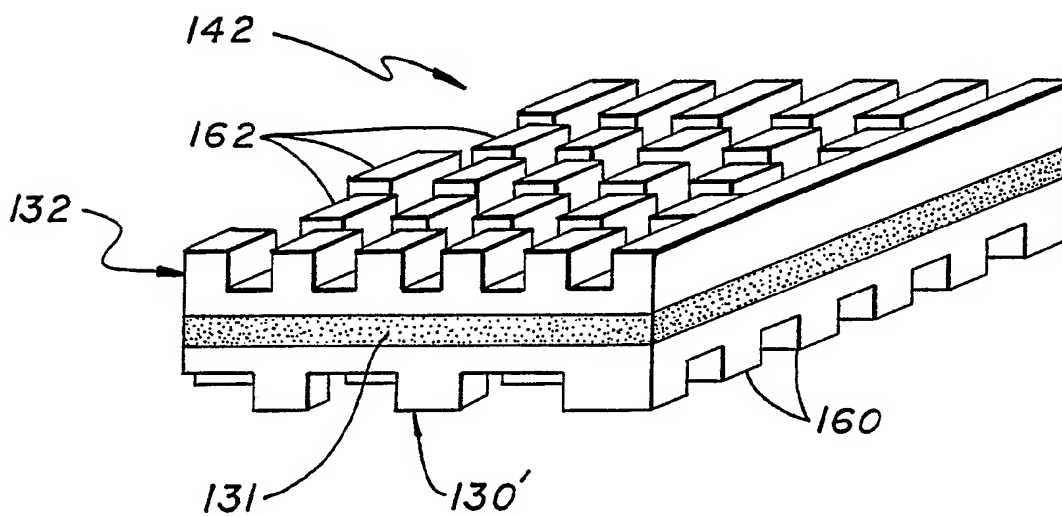


FIG. 7C

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/04854

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 H01M8/24; H01M8/12

II. FIELDS SEARCHEDMinimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	H01M

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸**III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹**

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	US,A,4 857 420 (D. L. MARICLE AND ALL) 15 August 1989 see column 1, line 66 - column 2, line 40 see column 2, line 51 - line 54 see column 5, line 3 - line 15	1,3,10, 11,14,19
Y	---	12,13
Y	US,A,4 883 497 (T. D. CLAAR AND ALL) 28 November 1989 see claims 1-9; figure 2	12
Y	---	
Y	EP,A,0 275 661 (ALLIED-SIGNAL INC.) 27 July 1988 see claims 1,3,4,8; figures 1-3B & US,A,4 816 036 28 March 1989 cited in the application	12,13

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¹⁰ Special categories of cited documents:^{"A"} document defining the general state of the art which is not considered to be of particular relevance^{"E"} earlier document but published on or after the international filing date^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)^{"O"} document referring to an oral disclosure, use, exhibition or other means^{"P"} document published prior to the international filing date but later than the priority date claimed^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.^{"A"} document member of the same patent family**IV. CERTIFICATION**

Date of the Actual Completion of the International Search

07 JANUARY 1992

Date of Mailing of this International Search Report

16 JAN 1992

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

D'HONDT J.W.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	CHEMICAL ABSTRACTS, vol. 114, no. 18, 6 May 1991, Columbus, Ohio, US; abstract no. 167843M, OGURA KAZUMI AND ALL: 'Solid-Electrolyte Fuel Cells' see abstract & JP,A,02 204 974 (MITSUBISHI HEAVY IND LTD) 14 August 1990 ---	5,7,15, 20
A	US,A,4 799 936 (B. RILEY) 24 January 1989 see claim 2 ---	10
A	PATENT ABSTRACTS OF JAPAN vol. 13, no. 509 (E-846)(3857) 15 November 1989 & JP,A,01 206 567 (MITSUBISHI HEAVY IND. LTD.) 18 August 1989 see abstract ---	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9104854
SA 51603

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 07/01/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4857420	15-08-89	None	
US-A-4883497	28-11-89	None	
EP-A-0275661	27-07-88	US-A- 4816036	28-03-89
		JP-A- 63239778	05-10-88
		US-A- 4913982	03-04-90
US-A-4816036	28-03-89	EP-A- 0275661	27-07-88
		JP-A- 63239778	05-10-88
		US-A- 4913982	03-04-90
JP-A-02204974	14-08-90	None	
US-A-4799936	24-01-89	None	